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**CORRELATION BETWEEN THERMODYNAMIC AND
KINETIC FRAGILITIES IN NON-POLYMERIC GLASS-
FORMING LIQUIDS (Preprint)**

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**Metals Development Section
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Correlation between thermodynamic and kinetic fragilities in non-polymeric glass-forming liquids

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ABSTRACT

A theoretical relationship between reduced excess heat capacity of super-cooled liquid

$\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ at the glass transition temperature T_g , fragility index m and reduced glass transition

temperature T_{rg} was derived for fragile non-polymeric glass-forming liquids under the assumptions that the fragile behavior of these liquids is described by the Vogel-Fulcher-Tammann (VFT) equation, the excess heat capacity of liquid is a hyperbolic function of the absolute temperature, and the VFT temperature T_0 is equal to the Kauzmann temperature T_K . It

was found that $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ is a complex function of m and T_{rg} , which indicates that the empirical

correlation $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m} = 0.025 m$ recently identified by Wang et al.¹ is probably valid only for

liquids which have nearly the same values of T_{rg} .

INTRODUCTION

In their recent work, Wang et al.¹ have analyzed behavior of 54 glass forming non-polymeric liquids and found an empirical correlation between the heat capacity step $\Delta C_p(T_g) =$

$C_p^{liquid}(T_g) - C_p^{glass}(T_g)$, which was measured at the glass transition temperature T_g and reduced by the entropy of fusion ΔS_m , with the liquid fragility index m . This correlation is shown in Figure 1 and can be expressed using the following relation:

$$\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m} = 0.025 m \quad (1)$$

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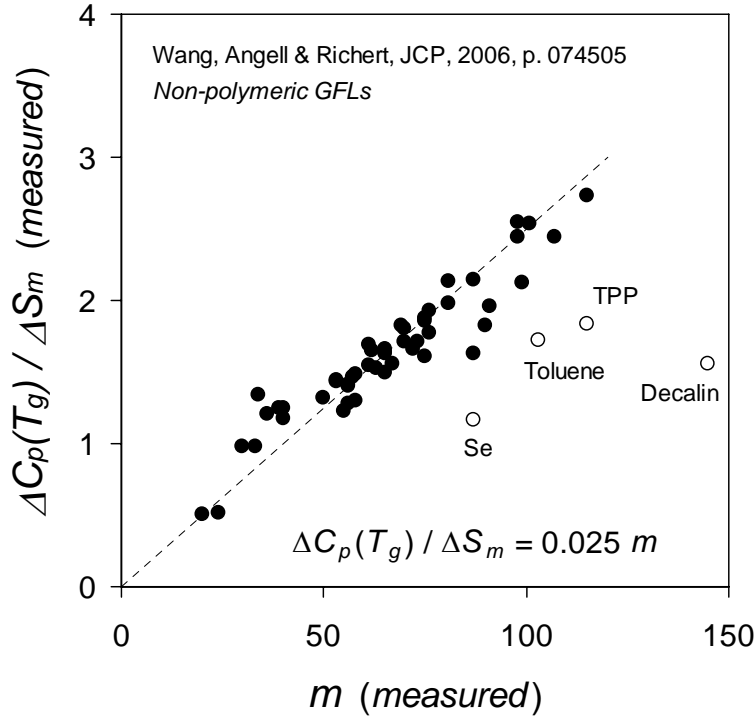


Figure 1. Correlation of the heat capacity jump at T_g to melting entropy ratio, $\Delta C_p(T_g)/\Delta S_m$, with kinetic fragility index, m , for 54 non-polymeric glass forming materials compiled by Wang et al.¹

The fragility index m , which is also called a kinetic fragility index or the steepness index, is defined as the slope of the curve $\log_{10} \tau$ vs T_g/T in a fragility plot at the glass transition temperature T_g .²

$$m = \left. \frac{d \log_{10} \tau}{d(T_g/T)} \right|_{T=T_g}, \text{ where } \tau \text{ is the Maxwell relaxation time and } T \text{ is the absolute temperature.}$$

Although relation (1) fits the most of the experimental data rather well (see Figure 1), several glass forming liquids such as selenium, toluene, triphenylphosphite (TPP) and decalin [decahydronaphthalene (DHN)] show large deviation from this simple dependence, which leads to a rather low coefficient of determination ($R^2 = 0.353$) of the fit of all data-points, and the authors of ref. [1] had difficulty to explain such ‘anomalous’ behavior.

In the present work, we have identified a theoretical relationship between $\Delta C_p(T_g)/\Delta S_m$ and m and found that $\Delta C_p(T_g)/\Delta S_m$ is not a single linear function of m , as relation (1) suggests, but it is a

composite function of both m and the reduced glass transition temperature $T_{rg} = T_g/T_m$.

Therefore, liquids with the same m but different T_{rg} values may have quite different $\Delta C_p(T_g)/\Delta S_m$ values, which explains the large deviation of several glass forming liquids from relation (1).

ANALYSIS

Thermodynamic Fragility

The heat capacity of the supercooled liquid, $C_p^{liquid}(T)$, is known to be higher than that of the respective crystal, $C_p^{crystal}(T)$. Because of this, the entropy of liquid, $S^{liquid}(T)$, decreases faster than that of crystal, $S^{crystal}(T)$, with a decrease in the temperature, which eventually would lead S^{liquid} to become smaller than $S^{crystal}$ below the Kauzmann temperature T_K .³ This entropy crisis is however avoided by liquid - glass transition at $T_g > T_K$, with the glass having nearly the same heat capacity as crystal. The excess heat capacity of the liquid, $\Delta C_p^{exc}(T) = C_p^{liquid}(T) - C_p^{crystal}(T)$, can therefore be determined as $\Delta C_p^{exc}(T) = T \frac{d\Delta S^{exc}(T)}{dT}$, where $\Delta S^{exc}(T) = S^{liquid}(T) - S^{crystal}(T)$.

The latter equation can be modified by the following way:

$$\frac{T_m}{T} \frac{\Delta C_p^{exc}(T)}{\Delta S_m} = \frac{d(\Delta S^{exc}/S_m)}{d(T/T_m)} \quad (2)$$

The right part of equation (2) describes the rate of change of ΔS^{exc} with a decrease in the temperature, or a slope of the so-called Kauzmann plot³ of $\Delta S^{exc}/S_m$ vs T/T_m , where T_m is the melting temperature. Correspondingly, the thermodynamic fragility index of a supercooled liquid, m_T , can be identified as the slope (or steepness) of the Kauzmann plot for this liquid at $T = T_g$:

$$m_T = \left. \frac{d(\Delta S^{exc}/S_m)}{d(T/T_m)} \right|_{T=T_g} \equiv \frac{T_m}{T_g} \frac{\Delta C_p^{exc}(T_g)}{\Delta S_m} \quad (3)$$

For a number of organic small molecule glass forming liquids, including those analyzed by

Wang et al.,¹ $\Delta C_p^{exc}(T) = \frac{A_I}{T}$,^{4,5,6} where A_I is a material constant, which can be determined using

a boundary condition: $\Delta S^{exc}(T_K) = 0$. Indeed, integrating Equation (2) in the range from T_K to T_m

gives $S_m = \int_{T_K}^{T_m} \frac{\Delta C_p^{exc}}{T} dT = K \frac{T_m - T_K}{T_m T_K}$, from which K is obtained as $K = \frac{T_m T_K}{T_m - T_K} S_m$ and

$$\Delta S^{exc} = \frac{T_m}{T} \frac{T - T_K}{T_m - T_K} S_m \quad (4)$$

$$m_T = \frac{T_m}{T_g} \frac{\Delta C_p^{exc}(T_g)}{\Delta S_m} = \left(\frac{T_m}{T_g} \right)^2 \frac{T_K}{T_m - T_K} \equiv T_{rg}^{-2} \frac{T_K / T_g}{T_{rg}^{-1} - T_K / T_g} \quad (5)$$

It can be seen from Equation (5) that the thermodynamic fragility (and, therefore, $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$)

increases when T_{rg} decreases and T_K/T_g increases.

Kinetic Fragility

The temperature dependence of the relaxation time of a supercooled liquid is generally well described by the Vogel-Fulcher-Tammann (VFT) equation,⁷ which modified logarithmic form reads:⁸

$$\log_{10} \left(\frac{\tau}{\tau_\infty} \right) = m_{\min} \frac{T_g - T_0}{T - T_0} \quad (6)$$

Here, T_0 is a VFT temperature at which $\tau \rightarrow \infty$; $\tau_\infty \approx 10^{-14} \text{ s}$ is the relaxation time at infinitely high temperature, $m_{\min} \equiv \log_{10}(\tau_g/\tau_\infty) \approx 16$; and $\tau_g = 100 \text{ s}$ is the relaxation time at T_g .

Differentiating Equation (6) by (T_g/T) at $T=T_g$, the kinetic fragility index is obtained as a function of T_g and T_0 :

$$m = m_{\min} \frac{T_g}{T_g - T_0} \quad (7)$$

From Equation (7) one may conclude that the kinetic fragility increases with an increase in T_0/T_g , but it does not depend on the melting temperature (or T_{rg}), which is quite different from the behavior of the thermodynamic fragility, Equation (5). One can therefore expect that, if it is

present, the relationship between m_T or $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ and m should also involve the reduced glass

transition temperature, T_{rg} .

Correlation between Kinetic and Thermodynamic Fragility Indexes

Comparing equations (5) and (7), one can conclude that the correlation between the kinetic and thermodynamic fragility indexes has effect only if the characteristic temperatures T_0 and T_K are dependent parameters. Rationalization for this correlation comes from the Adams-Gibbs theory,⁹ which predicts a dependence of the relaxation time on the liquid configurational entropy, S_{conf} ,

$$\log_{10}\left(\frac{\tau}{\tau_{\infty}}\right) = \frac{A}{TS_{conf}(T)} \quad (7)$$

The parameter A in Equation (7) can be shown to equal $A = m_{min} T_g S_{conf}(T_g)$. Comparing Equations (5) and (7) leads to the following temperature dependence of S_{conf} :

$$S_{conf}(T) = \frac{T_g}{T} \frac{T - T_0}{T_g - T_0} S_{conf}(T_g) \equiv \frac{T_m}{T} \frac{T - T_0}{T_m - T_0} S_{conf}(T_m) \quad (8)$$

It has been widely assumed that S_{conf} is equal or at least proportional to ΔS^{exc} (i.e. $S_{conf} \cong a \Delta S^{exc}$, where a is a constant),¹⁰ which can hold only if $T_0 = T_K$ [e.g. compare Equations (4) and (8)]. Although the assumption $S_{conf} \cong a \Delta S^{exc}$ has recently been discussed to be problematic^{11,12} and a large difference between T_0 and T_k has been found for strong glass-forming liquids, including bulk metallic glasses,¹³ compilation of a number of experimental data^{14,15} shows that the relation $T_0 \cong T_k$ is indeed valid for many fragile liquids, including non-polymeric liquids. Assuming that $T_0 \cong T_k$ for the liquids analyzed by Wang et al.,¹ and combining Equations (5) and (7), one can find the following correlation between m_T and m :

$$m_T = \frac{1}{T_{rg}} \frac{m - m_{min}}{m(1 - T_{rg}) + m_{min} T_{rg}} \quad (9)$$

Taking into account relation between m_T and $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$, Equation (3), one can obtain the

relationship between $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ and the kinetic fragility m :

$$\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m} = \frac{m - m_{min}}{m(1 - T_{rg}) + m_{min} T_{rg}} \quad (10)$$

As it was expected, both m_T and $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ are functions of both m and T_{rg} .

Validation of Equation (10) with Experimental Data

When the empirical relation, Equation (1), is compared with the theoretical relation, Equation (10), a rather large difference can be seen. Indeed, Equation (1) identifies a linear dependence between $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ and m , while Equation (10) predicts a non-linear dependence between these

parameters, with $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ approaching the value of $(1-T_{rg})^{-1} \approx 3.0$ when $m \rightarrow \infty$. Moreover,

Equation (10) predicts that $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ is a function of both m and T_{rg} , so that the glass forming

liquids with the same m but different T_{rg} should have different values of $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$. The analysis

of Equation (10) shows that $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ increases with an increase in m and a decrease in T_{rg} .

Figure 2 shows the dependence of the experimentally measured and calculated (using equation 10 and experimental data for m and T_{rg}) values of $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ for 54 liquids from Table 1 of ref

[1]. It can be seen that Equation (10) describes the correlation between $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$, m and T_{rg}

much better than Equation (1). TPP, decalin and toluene are now in line with other glass-forming liquids and the coefficient of determination of the fit is $R^2 = 0.801$. Selenium still deviates from

the linear fit of the $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ (experimental) vs $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ (calculated); however the deviation

now is much smaller than in the case of the fit by Equation (1) (compare Figures 1 and 2).

In conclusion, a theoretical relationship between $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$, m and T_{rg} , Equation (10), was

derived for fragile glass-forming liquids under the assumptions that (a) fragile behavior of these liquids is described by the VFT equation, (b) the excess heat capacity of liquid is inversely proportional to the absolute temperature, and (c) the VFT temperature T_0 is equal to the

Kauzmann temperature T_K . It was found that $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ is a complex function of m and T_{rg} ,

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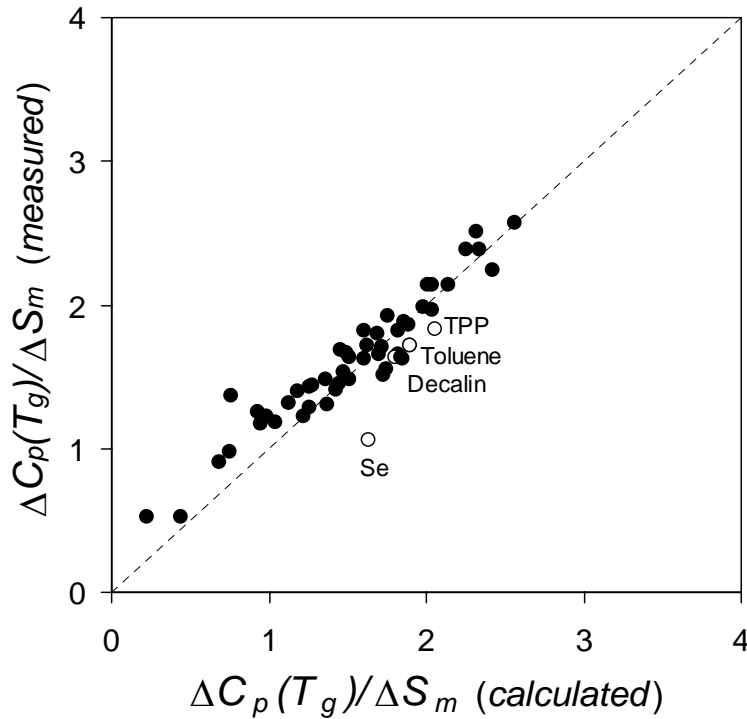


Figure 2. Experimentally measured vs calculated (using Equation 10) values of $\frac{\Delta C_p^{exc}(T_g)}{\Delta S_m}$ for 54 glass forming liquids from Table 1 of Ref. [1] (see also Figure 1).

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